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(54) Title: RADIATION CURABLE PRESSURE SENSITIVE HOT MELT ADHESIVE

(57) Abstract

A pressure sensitive hot melt adhesive is prepared containing a depolymerized elastomeric polymer of relatively low molecular weight, and an elastomeric polymer of relatively high molecular weight as the base polymer blend together with a tackifying resin and a plasticizer. The adhesive which is a semi-liquid at room temperature, may be applied to substrates such as self-adhesive labels at moderate temperatures (260 °F), and after crosslinking with ultraviolet or electron beam radiation gives a pressure sensitive adhesion with good low temperature (–20 °F) as well as room temperature (68 °F) properties.

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RADIATION CURABLE PRESSURE SENSITIVE HOT MELT ADHESIVE

BACKGROUND OF THE INVENTION

The present invention relates to hot melt adhesives, and more particularly, to a method of utilizing radiation to improve the properties of pressure sensitive hot melt adhesives used in the manufacture of articles such as self-adhesive labels, and to the pressure sensitive adhesive composition itself.

Typically, a hot melt adhesive may be advantageously used to bond various substrates together since there is no evaporation step necessary during manufacture, as would be the case for water-based or solvent-based adhesives. Suitable hot melt adhesives must possess the appropriate bond strength to adhere the substrates involved, and must also possess good flexibility, no staining or bleedthrough, suitable viscosity and open time to function on commercial equipment, acceptable stability under storage conditions, and acceptable thermal stability under normal application conditions.

Many different polymers have been used in hot melt adhesives. In this regard, typical hot melt adhesives have employed polymers which have included S-I-S (styrene-isoprene-styrene); SBS (styrene-butadiene-styrene); SEBS (styrene-ethylene-butylene-styrene); EVA (ethylene-vinyl-acetate); and APAO (amorphous-poly-alpha-olefin). While these polymers, when properly blended, provide acceptable adhesion between most substrates, multicomponent polymer systems which form pressure sensitive adhesives have unique limitations. One major deficiency of pressure sensitive hot melt adhesives is to have acceptable elevated temperature cohesive strength. Radiation cure or crosslinking generated by electron beam (EB) radiation or by actinic radiation such as ultraviolet (UV) radiation has been used to enhance cohesive properties of these adhesives, especially to improve elevated temperature shear performance. Normally, the adhesive is applied to facestock and/or a release liner and

subjected to a suitable curing action to improve such property by passing the adhesive coated substrate under an irradiating device for a sufficient amount of time depending upon the degree of curing desired.

Another shortcoming of radiation curable pressure sensitive hot melt adhesives is that although an adhesive coated facestock and/or release liner can readily sustain relatively high radiation doses, i.e. up to about 100 kilo Gray (kGy), higher doses may create degradation of various components of adhesive labels and/or tape constructions. Also, adverse reactions may result between the adhesive and the silicone release agent of the release liner. Thus, a balance between line speed, radiation dose and desired degree of curing must be made on a case-by-case basis. If a particular adhesive composition requires too much radiation, it will reduce the line speed at which an adhesive coated facestock or release liner can pass under an irradiating device or will require a greater number of irradiating devices, both of which are costly and therefore undesirable.

Radiation curable pressure sensitive hot melt adhesives are known in the art. Attempts to formulate improved radiation curable adhesives are disclosed in U.S. Patents 4,948,825 and 5,115,008.

SUMMARY OF THE INVENTION

The present invention provides an improved pressure sensitive hot melt adhesive for use on substrates such as label facestock and/or a release liner therefor. The improvement resides in the use of a depolymerized elastomeric polymer in combination with a relatively high molecular weight elastomeric polymer and a tackifying resin. It has been discovered that by depolymerizing an elastomeric polymer, an improved pressure sensitive hot melt adhesive may be obtained having enhanced cohesive properties, especially improved elevated temperature shear strength. The adhesive is semi-liquid at room temperature, and thus may be applied to substrates at moderate temperatures (260°F) and crosslinked with ultraviolet or electron beam radiation to provide a

pressure sensitive adhesive with good low temperature (-20°F) and room temperature (68°F) properties.

In one aspect of the invention, a method of making a pressure sensitive hot melt adhesive is disclosed comprising the steps of depolymerizing an elasomeric polymer, mixing the depolymerized elastomeric polymer with a relatively high molecular weight elastomeric polymer and a tackifying resin to form an adhesive mixture, applying the adhesive mixture to a substrate to form a coated substrate, and irradiating the coated substrate to cure the adhesive mixture and provide a pressure sensitive adhesive thereon. The step of depolymerizing preferably comprised kneading the elastomeric polymer into a liquid state prior to mixing with the remaining ingredients although any method of depolymerizing the elastomeric polymer may be utilized.

In another aspect of the invention, there is provided a pressure sensitive adhesive composition which comprises, in combination, from about 10% to 90% of a depolymerized elastomeric polymer, from about 10% to 90% of a relatively high molecular weight elastomeric polymer, from about 10% to 70% of a tackifying resin, from about 0% to 50% of a plasticizer, and about 0% to 10% of a crosslinker, with the ingredients comprising or adding up to 100% by weight of the adhesive composition. Optional additives may be incorporated into the adhesive composition in order to modify particular physical properties, and an anti-oxidant may be employed, as is conventional, as a stabilizer. If ultraviolet light is employed as the source of radiation, the composition should further include a photoinitiator although a photoinitiator is not absolutely required. Preferably, a polyisoprene is used as the depolymerized elastomeric polymer as well as the high molecular weight elastomeric polymer, and the tackifying resin is a hydrocarbon resin.

The resultant adhesive has a lower application temperature and better flowout properties compared to conventional hot melt pressure

sensitive adhesives. In addition, after radiation curing, the adhesive has good low temperature to room temperature properties.

DETAILED DESCRIPTION OF THE INVENTION

A pressure sensitive hot melt adhesive composition having ingredients in the following ranges provides a radiation curable adhesive in accordance with the present invention. More particularly, the adhesive composition useful in the present invention has the following ingredients by weight;

about 10-90% of a depolymerized elastomeric polymer, preferably polyisoprene;

about 10-90% of a high molecular weight polymer, preferably polyisoprene;

about 10-70% of a tackifying resin, preferably a hydrocarbon resin;

about 0-50% of a plasticizer;

0-10% of a crosslinker or curing agent;

0-10% of a photoinitiator if UV radiation is employed; and

about 0.1-2% of an antioxidant; the components totaling 100% by weight.

Any of a variety of available thermoplastic materials can be used as the polymer or in blends in the radiation curable compositions in an amount from about 10% to about 90% by weight, preferably from about 15% to about 40%. Examples of such materials include ethylene based polymers, including ethylene/vinyl acetate, ethylene acrylate, ethylene methacrylate, ethylene methyl acrylate, ethylene methyl methacrylate, ethylene vinyl acetate carbon monoxide, and ethylene N-butyl acrylate carbon monoxide, polybutylene, polyisoprene, high and low density polyethylene, polyethylene blends and chemically modified polyethylene, copolymers of ethylene and 1-6 mono- or di-unsaturated monomers, polyamides, polybutadiene rubber, polyesters such as polyethylene terephthalate, polybutylene terephthalate; thermoplastic polycarbonates,

atactic polyalphaolefins, including atactic polypropylene, polyvinylmethylether and others; thermoplastic polyacrylamides, polyacrylonitrile, copolymers of acrylonitrile and other monomers such as butadiene styrene; polymethyl pentene, polyphenylene sulfide, aromatic polyurethanes; styrene-acrylonitrile, acrylonitrile-butadiene-styrene, styrene-butadiene rubbers, acrylontrile-butadiene-styrene elastomers, polyphenylene sulfide, A-B, A-B-A, A-$(B-A)_n$-B, $(A-B)_n$-Y block polymers wherein the A block comprises a polyvinyl aromatic block such as polystyrene, the B block comprises a rubbery midblock which can be hydrogenated, such as polybutadiene or polyisoprene, Y comprises a multivalent compound, and n is an integer of at least 3, and mixtures of said substances.

While the total styrene content of the polymers can be as much as 51 wt-% of the polymer, and since the polymers can have more than two A blocks for optimal performance, the total A block should be less than or equal to about 45 wt-% of the polymers, and, most preferably, is less than or equal to 35 wt-% of the polymer. In an S-B-S (styrene-butadiene-styrene) copolymer, the preferred molecular weight is about 50,000 to 120,000, and the preferred styrene content is about 20 to 45 wt-%. In an S-I-S (styrene-isoprene-styrene) copolymer, the preferred molecular weight is about 100,000 to 200,000 and the preferred styrene content is about 14-35 wt-%. Hydrogenating the butadiene midblocks produces rubbery midblocks that are typically converted to ethylene-butylene midblocks.

Such block copolymers are available from Shell Chemical Company, Enichem, Fina and Dexco. Multiblock or tapered block copolymers (the A-$(B-A)_n$-B type) are available from Firestone.

Preferred polymers for use in the radiation curable adhesive as either or both the depolymerized elastomeric polymer or the high molecular weight elastomeric polymer are based on unsaturated natural and synthetic elastomeric polymers including, but not limited to, block, random or multiarmed copolymers and mixtures thereof. The preferred

unsaturated elastomeric polymers are natural rubber, polybutadiene, polyisoprene, butyl rubber, ethylene propylene diene rubbers, styrene-butadiene block copolymers, styrene-butadiene-styrene block copolymers, styrene-isoprene block copolymers, styrene-isoprene-styrene block copolymers, multiarmed styrene-isoprene block copolymers and the like.

Particularly useful elastomeric block polymers to which the invention is directed are ABA block or multiarmed $(AB)_x$ block copolymers, wherein x has a value of 2 or more and mixtures thereof and wherein A is a block comprising at least one monoalkenyl arene, preferably styrene, alpha methyl styrene, vinyl toluene and the like, and B is an elastomeric conjugated diene block such as a polybutadiene or a polyisoprene block with polyisoprene blocks preferred.

More preferably, the elastomeric copolymers are formed of styrene-butadiene-styrene block copolymers and/or styrene-isoprene-styrene block, multiarmed styrene-isoprene block copolymers, polybutadiene and polyisoprene. Mixtures of elastomers may be employed.

The elastomeric base copolymers are not normally pressure sensitive adhesives and pressure sensitive adhesive properties are induced by the addition of other hydrocarbon materials known as tackifiers.

The tackifying resins or tackifiers which are used in the adhesives of the present invention are those which extend the adhesive properties and improve the specific adhesion of the polymer. As used herein, the term "tackifying resin" and/or "tackifiers" includes:

(a) natural and modified rosin such as, for example, gum rosin, wood rosin, tall-oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin and polymerized rosin;

(b) glycerol and pentaerythritol esters of natural and modified rosins, such as, for example, the glycerol ester of pale wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of pale wood rosin, the pentaerythritol ester of

hydrogenated rosin, the pentaerythritol ester of tall oil rosin and the phenolic modified pentaerythritol ester of rosin;

(c) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 60°C to 140°C, the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins;

(d) copolymers and terpolymers of natural terpenes, e.g. styrene/terpene, α-methyl styrene/terpene and vinyl toluene/terpene;

(e) phenolic-modified terpene resins such as, for example, the resin product resulting from the condensation, in an acidic medium, of a terpene and a phenol;

(f) aliphatic petroleum hydrocarbon resins having Ring and Ball softening points of from about 60° to 140°C, the latter resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; examples of such commercially available resins based on a C_5-olefin fraction of this type are "Wingtack 95" and "Wingtack 115" tackifying resins sold by Goodyear Tire and Rubber Company;

(g) aromatic petroleum hydrocarbons and the hydrogenated derivatives thereof;

(h) aliphatic/aromatic petroleum derived hydrocarbons and the hydrogenated derivatives thereof.

Mixtures of two or more of the above described tackifying resins may be required for some formulations. Although a range of 10-70% by weight tackifying resin may be used, the preferred range is 30% to 60%. Compositions containing less than about 30% by weight resin do not have sufficient initial adhesion, while compositions with greater than about 70% by weight resin have too low of a cohesive strength even after curing or crosslinking. An example of a commercially available tackifying resin which

is useful for the present invention includes the resin which is identified commercially by the trade designation Escorez 5300. This resin is a hydrocarbon resin, and is available from Exxon Chemical Company.

A plasticizer can be present in the composition of the present invention in amounts of about 0% to about 50% by weight, preferably from about 10% to about 30%, in order to provide desired viscosity control without substantially decreasing the adhesive strength or the service temperature of the adhesive. A suitable plasticizer may be selected from the group which not only includes the usual plasticizing oils, such as mineral oil, but also olefin oligomers and low molecular weight polymers, glycol benzoates, as well as vegetable and animal oil and derivatives of such oils. The petroleum derived oils which may be employed are relatively high boiling temperature materials containing only a minor proportion of aromatic hydrocarbons. In this regard, the aromatic hydrocarbons should preferably be less than 30%, and more particularly less than 15%, by weight, of the oil. Alternately, the oil may be totally non-aromatic. The oligomers may be polypropylenes, polybutenes, hydrogenated polyisoprene, hydrogenated butadiene, or the like having average molecular weights between about 350 and about 10,000. Suitable vegetable and animals oils include glycerol esters of the usual fatty acids and polymerization products thereof. Other plasticizers may be used provided they have suitable compatibility and microwave absorption characteristics. The plasticizer that finds usefulness in the present invention can be any number of different plasticizers but Hydrobrite 550, a mineral oil available from Witco, has also been found to be an appropriate plasticizer. As will be appreciated, plasticizers have typically been employed to lower the viscosity of the overall adhesive composition without substantially decreasing the adhesive strength and/or the service temperature of the adhesive.

Waxes can be used in the composition of the present invention in amounts between 0-30%, and are used to reduce the melt viscosity of the hot melt construction adhesives without appreciably decreasing their

adhesive bonding characteristics. These waxes also are used to reduce the open time of the composition without effecting the temperature performance. Among the useful waxes are:

(1) low molecular weight, that is, 1000-6000, polyethylene having a hardness value, as determined by ASTM method D-1321, of from about 0.1 to 120 and ASTM softening points of from about 150° to 250° F:

(2) petroleum waxes such as paraffin wax having a melting point of from about 130° to 170° F and microcrystalline wax having a melting point of from about 135° to 200° F, the latter melting points being determined by ASTM method D127-60;

(3) atactic polypropylene having a Ring and Ball softening point of from about 120° to 160° C;

(4) synthetic waxes made by polymerizing carbon monoxide and hydrogen such as Fischer-Tropsch wax; and

(5) polyolefin waxes. As used herein, the term "polyolefin wax" refers to those polymeric or long-chain entities comprised of olefinic monomer units. These materials are commercially available from Eastman Chemical Co. under the trade name "Epolene." The materials which are preferred to use in the compositions of the present invention have a Ring and Ball softening point of 200° F to 350° F. As should be understood, each of these wax diluents is solid at room temperature. Other useful substances include hydrogenated animal, fish and vegetable fats and oils such as hydrogenated tallow, lard, soya oil, cottonseed oil, castor oil, menhadin oil, cod liver oil, etc., and which are solid at ambient temperature by virtue of their being hydrogenated, have also been found to be useful with respect to functioning as a wax diluent equivalent. These hydrogenated materials are often referred to in the adhesives industry as "animal or vegetable waxes." Additionally, hydrocarbon oils, especially naphthenic or paraffinic process oils, may also be employed herein as the wax diluent.

The present invention includes a stabilizer or antioxidant in an amount of from about 0.1% to about 2% by weight, but preferably from about 0.1% to 1%. The stabilizers which are useful in the hot melt adhesive compositions of the present invention are incorporated to help protect the polymers noted above, and thereby the total adhesive system, from the effects of thermal and oxidative degradation which normally occurs during the manufacture and application of the adhesive as well as in the ordinary exposure of the final product to the ambient environment. Such degradation is usually manifested by a deterioration in the appearance, physical properties and performance characteristics of the adhesive. A particularly preferred antioxidant is Irganox 1010, a tetrakis(methylene(3,5-di-teri-butyl-4-hydroxyhydrocinnamate))methane manufactured by Ciba-Geigy. Among the applicable stabilizers are high molecular weight hindered phenols and multifunctional phenols, such as sulfur and phosphorus-containing phenols. Hindered phenols are well known to those skilled in the art and may be characterized as phenolic compounds which also contain sterically bulky radicals in close proximity to the phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to the phenolic hydroxyl group. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency and correspondingly, its reactivity; this steric hindrance thus providing the phenolic compound with its stabilizing properties. Representative hindered phenols include:

1,3,5-trimethyl-2,4,6-tris(3-5-di-tert-butyl-4-hydroxybenzyl) benzene;

pentaerythritol tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenyl) propionate;

n-octadecyl-3(3,5-ditert-butyl-4-hydroxyphenyl) propionate;

4,4'-methylenebis(4-methyl-6-tert butylphenol);

4,4'-thiobis(6-tert-butyl-o-cresol);

2,6-di-tert-butylphenol;

6- (4-hydroxyphenoxy)-2,4-bis(n-ocytlthio)-1,3,5-triazine;

2,4,6-tris(4-hydroxy-3,5-di-tert-butyl-phenoxy)-1,3,5-triazine;

di-n-octadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate;

2-(n-octylthio)ethyl-3,5-di-tert-butyl-4-hydroxybenzoate; and

sorbitol hexa-(3,3,5-di-tert-butyl-4-hydroxy-phenyl) propionate.

Especially preferred as a stabilizer is pentaerythritol tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenol) propionate.

The performance of these stabilizers may be further enhanced by utilizing, in conjunction therewith; (1) synergists such as, for example, as thiodipropionate esters and phosphites; and (2) chelating agents and metal deactivators as, for example, ethylenediaminetetraacetic acid, salts thereof, and disalicylalpropylenediimine.

Crosslinkers which are multifunctional monomers such as acrylates and methacrylates are thermally reactive. The process to achieve cure requires in-line mixing to avoid premature crosslinking independent of the ultimate means of cure. Polythiol crosslinkers, for instance, are functional at concentrations of about 10% or less by weight of the total composition. The polythiol cross-linkers include for instance, pentaerythritoltetrathioglycolate, pentaerythritol-tetra(3-mercaptopropionate), trimethylolethanetrimercaptopropionate, trimethylolpropanetrithioglycolate, trimethylolpropane tri(3-mercaptopropionate) and the like.

As with the multifunctional acrylates and methacrylates, the polythiol cross-linkers are preferably added to the composition by in line mixing. The purpose is to avoid premature crosslinking before radiation curing the pressure sensitive adhesive composition.

Any standard photoinitiator may be employed as long as it is compatible with the other ingredients of that composition.

The end composition is useful for labels, tape, etc. and may be formulated using any of the techniques known in the art. A representative example of the prior art procedure involves placing all of

the ingredients, in a jacketed mixing kettle, and preferably in a jacketed heavy duty mixer of the Baker-Perkins or Day type, and which is equipped with rotors, and thereafter raising the temperature of this mixture to a range of about 250° F to 350° F. It should be understood that the precise temperature to be used in this step would depend on the melting point of the particular ingredients. The resulting adhesive composition is agitated until a homogeneous mixture is obtained and the polymers completely dissolve. A vacuum is then applied to remove any entrapped air.

As a preliminary step, and before the final mixing referred to above, a high molecular weight elastomeric polymer to be used in the end composition is kneaded into semi-liquid form having cold flow properties. Such elastomeric polymers are normally solid at room temperature, and it has been discovered that kneading the elastomeric polymer "depolymerizes" the polymer, i.e. breaks up the long chain molecules into shorter chain molecules to form a semi-liquid form having cold flow properties at room temperature (68°F). Any mechanical means may be used to depolymerize the polymer, and typically this will result in a reduction of molecular weight from $\overline{M}w$ 1,000,000 or more to about $\overline{M}w$ 100,000 or less. Once the polymer is depolymerized, the depolymerized polymer is added to the remaining ingredients and homogeneously mixed therewith as discussed previously.

Optional additives may be incorporated into the adhesive composition in order to modify particular physical properties. These additives may include colorants, such as titanium dioxide and fillers such as talc and clay.

The invention is further illustrated by way of the examples which are set forth below.

EXAMPLE 1

The following composition was prepared by first kneading the Natsyn until depolymerized, and then adding the remaining ingredients.

Parts by Wt	Description	Tradename	Vendor
15.0	Mineral Oil	Hydrobrite 550	Witco
55.0	Hydrocarbon Resin	Escorez 5300	Exxon Chemical Co.
1.0	Photoinitiator (Benzyl Dimethyl Ketal)	Sartomer KB-1	Van Waters & Rogers
7.5	Polyisoprene	Natsyn 2210	Goodyear Chemicals
22.5	Polyisoprene	Isolene 400	Hardman
.2	Antioxidant	Irganox 1010-DD	Ciba Speciality
1.5	Curing Agent	Trimethylol-propane Tri 3 (TMPTMP)	Hampshire Chemical Co.

The resultant adhesive functioned well on a self-adhesive label.

EXAMPLES 2-11

The following compositions were prepared by first kneading the Natsyn until depolymerized, and then adding the remaining ingredients. All ingredients are reported in parts by weight.

	2	3	4	5	6
Isolene 400	32.50	22.50	22.50	12.50	22.50
Natsyn 2210	7.50	7.50	7.50	7.50	7.50
Escorez 5300	50.00	50.00	60.00	60.00	55.00
Hydrobrite 550	10.00	20.00	10.00	20.00	15.00
Irganox 1010	0.20	0.20	0.20	0.20	.20
KB1 (photoinitiator)	1.00	1.00	1.00	1.00	1.00
TMPTMP	1.50	1.50	1.50	1.50	1.50

	7	8	9	10	11
Isolene 400	27.50	17.50	17.50	7.50	20.00
Natsyn 2210	12.50	12.50	12.50	12.50	10.00
Escorez 5300	50.00	50.00	60.00	60.00	55.00
Hydrobrite 550	10.00	20.00	10.00	20.00	15.00
Irganox 1010	0.20	0.20	0.20	0.20	0.20
KB1 (photoinitiator)	1.00	1.00	1.00	1.00	1.00
TMPTMP	1.50	1.50	1.50	1.50	1.50

To establish product properties standard 180° Peel, Loop tack, Loop tack at 40°F and SAFT (°F) tests were performed in accordance with the ASTM standards for each test. The results are reported in Table 1.

TABLE 1

Mix	180° Peel	Loop Tack	40°F Loop Tack	SAFT (°F)
2	4.6, 4.1, 3.5 cohesion failure	4.06, 3.76 smooth	7.29 zippy	121, 181, 138
3	3.0, 2.2 cohesion failure	2.86; smooth 4.70; slightly stringy	6.42, 7.65 smooth	115, 121
4	3.9, 3.4 cohesion failure	6.46, 7.04 smooth	1.11; zippy 4.81; zippy	135, 129
5	3.5, 3.9 cohesion failure	9.21; slightly stringy 6.09; smooth	5.55, 2.59 zippy	128, 134
6	4.0, 3.9 cohesion failure	5.68, 5.42 smooth	7.17; smooth 5.12; zippy	119, 120
7	4.1, 4.5 cohesion failure	5.48, 4.52 smooth	4.52, 5.48 zippy	140, 152

Mix	180° Peel	Loop Tack	40°F Loop Tack	SAFT (°F)
8	2.5, 2.6 cohesion failure	3.46, 4.00 smooth	6.51, 6.49 zippy	164, 169
9	3.4, 5.1 cohesion failure	5.61, 7.08 smooth	1.30, 2.23 zippy	152, 155
10	4.3, 3.6 cohesion failure	6.56; slightly stringy 5.43; smooth	5.76 zippy	149, 150
11	4.2, 4.0 cohesion failure	5.35, 3.54 smooth	2.55, 1.41 zippy	137, 135

In summary, the best refrigeration grade sample is mix #6 because it has a good viscosity and a good balance of room temperature and low temperature properties.

CLAIMS

We claim:

1. A method of making a pressure sensitive hot melt adhesive, comprising the steps of:

depolymerizing an elastomeric polymer;

mixing said depolymerized elastomeric polymer with a relatively high molecular weight elastomeric polymer and a tackifying resin to form an adhesive mixture;

applying said adhesive mixture to a substrate to form a coated substrate; and

irradiating said coated substrate to cure said adhesive mixture and provide a pressure sensitive adhesive.

2. The method of claim 1 wherein the step of depolymerizing comprises kneading an elastomeric polymer into a semi-liquid state having cold flow properties.

3. The method of claim 1 wherein the step of irradiating comprises dosing the coating substrate with electron beam radiation or ultraviolet radiation.

4. The method of claim 1 wherein the substrate is selected from the group consisting of a label and a release liner.

5. The method of claim 1 wherein the tackifying resin is a hydrocarbon resin.

6. The method of claim 1 wherein the depolymerized elastomeric polymer is a polyisoprene.

7. The method of claim 1 wherein the high molecular weight elastomeric polymer is a polyisoprene.

8. A pressure sensitive hot melt adhesive, comprising:

about 10% to 90% of a depolymerized elastomeric polymer;

about 10% to 90% of a relatively high molecular weight elastomeric polymer;

about 10% to 70% of a tackifying resin;

about 0% to 50% of a plasticizer; and

about 0% to 10% of a crosslinker;

the ingredients comprising 100% by weight of the adhesive.

9. The adhesive of claim 8, further including about 0.1% to 2% of an antioxidant.

10. The adhesive of claim 8, further including up to 10% of a photoinitiator.

11. The adhesive of claim 8, wherein the tackifying resin is a hydrocarbon resin.

12. The adhesive of claim 8, wherein the depolymerized elastomeric polymer is a polyisoprene.

13. The adhesive of claim 8, wherein the high molecular weight elastomeric polymer is a polyisoprene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/26399

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J121/00 C09J109/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US T958004 I (FIRESTONE TIRE & RUBBER) 3 May 1977 (1977-05-03) *abstract*	8-13
X	GB 405 263 A (MINNESOTA MINING & MANUFACTURING COMPANY) claim 4; example C	9
X	DE 28 03 944 A (KURARAY CO) 31 August 1978 (1978-08-31)	8
Y	claims 1-7	8-13
X	US 5 760 135 A (KORPMAN DENNIS ET AL) 2 June 1998 (1998-06-02)	1,5,8,9, 11-13
Y	column 4, line 30-37 claims 1-13 column 5, line 34-48; table B	8-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search: 28 March 2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/26399

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